

ELECTROCHEMICAL FUNCTIONALIZATION OF LINEAR ALKYL BENZENES IN ACETIC ACID

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Anodic acetoxylation is an alternative way to functionalise an aromatic compound <sup>(1)</sup>. Preparative acetoxylation has been used as a tool to prepare chemicals such as preservers, herbicides, medicines <sup>(2)</sup>, since chemical synthesis is quite difficult to control the reaction and electrochemistry offers a selective, clean way to prepare fine chemicals. Electrochemical acetoxylation was widely studied during the 70's based on the well known Kolbe reaction, these studies suggested that acetoxy radicals were probably generated in the Kolbe reaction, but they were not involved in the formation of acetate-aromatics, since the aromatics reported in literature undergoes acetoxylation at potentials below the oxidation potential of the acetate ion. Acetoxylation of alkyl aromatics involves the initial 2e<sup>-</sup> transference step and a further deprotonation step to produce the benzyl cation.

In this work, evaluation of the electrochemical response of several alkylbenzenes (ethylbenzene, phenylhexane, phenylheptane, phenyloctane and phenylnonane) within a wide potential range in acetic acid/sodium acetate on a platinum electrode is discussed. The aim of this work was to functionalise alkylbenzenes using acetoxy as a nucleophyle, the determination of kinetic parameters, and the establishment of a correlation between these parameters and the structure and mechanistic aspects of their electrochemical acetoxylation.

An evaluation of cyclic voltammetries performed either under static or hydrodynamic conditions gives us information related to the type of electrochemical mechanism involved. The diagnostic plots, taken from cyclic voltammetry, on a static electrode, suggests that an EC type of mechanism is involved in the oxidation of ethylbenzene, phenylheptane and phenyloctane. For the phenylhexane, however, an EC process, associated to the first oxidation peak and a diffusion controlled electron transference for the second oxidation peak is observed. Phenylnonane shows an adsorption process followed by an EC process at the second peak. Levich plots suggest an (EC) type of mechanism for the ethylbenzene, phenylheptane and phenyloctane. For the phenylhexane and the phenylnonane, however, an ECE process was followed.

Table I resume the results: diffusion coefficient, number of electrons (n), apparent activation energy (ΔH\*) and heterogeneous rate constant (k).

Table I

React.	Reaction Order	D(cm <sup>2</sup> /s) x10 <sup>-5</sup>	n(e <sup>-</sup> )	ΔH* J/mol	k (cm/s)x 10 <sup>-2</sup>
ArC <sub>2</sub> H <sub>5</sub>	0.80	1.00	2.00	3.47	-
ArC <sub>6</sub> H <sub>13</sub>	0.70	0.82	1.52	2.92	0.79
ArC <sub>7</sub> H <sub>15</sub>	0.52	0.63	1.49	2.81	0.50
ArC <sub>8</sub> H <sub>17</sub>	0.60	0.38	1.86	2.72	1.30
ArC <sub>9</sub> H <sub>19</sub>	0.87	0.20	2.09	2.77	3.40

SE = static electrode RDE = rotating disc electrode

Our results suggest that the reaction mechanism involved is not so complex and the coupled chemical reaction (i.e. nucleophylic attack, deprotonation, etc.) is quite fast . In an earlier work<sup>(3)</sup>, we reported a general scheme of oxidation for alkylbenzenes, assuming an ECE type of mechanism, with a nucleophylic attack to the carbonium ion formed after the second electron transference. In our case, we may have a competition between both ring and side chain of nucleophylic attack for the acetoxylation, and one of these pathways dominates the other, depending on the homogeneous rate constant (deprotonation) since it will affect the second electron transference, which yields the carbonium ion. The analysis of products showed for the alkylbenzenes with chains containing more than six atoms of carbon, that the main product exhibited a ring substitution, while those with shorter chains, are equally functionalised either on the side chain or on the aromatic ring; being the nucleophylic attack by the acetate ion, a fast reaction in both cases. As the potential increased, the yield increased, at potentials higher than 1.80 V vs. Ag/Ag<sup>+</sup>, oxidation of the acetate ion occurs, suppressing the formation of product. Evidences of nucleophylic substitution on the ring have been obtained from IR and Mass studies.

According to our results, for ethylbenzene, in those mechanisms assigned as an EC mechanism, the rate determining step is the nucleophylic attack of an acetate ion to the cation radical, with a rapid loss of a proton and an electron, and this could be the reason why the second electron transference cannot be observed on the time scale of our experiments. Phenylhexane and phenylnonane, clearly showed the crossover region, which corresponds to the coupled chemical reaction between the two electron transferences, for an ECE type of mechanism. In the case of phenylhexane, when the electrolysis is performed at the difusional region of the second wave, we obtain

a combination of chain and ring substitution processes, but when the electrolysis is run at the first wave diffusion region, the substitution on the ring is the main route.

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